The ASU-ISU collaboration on low temperature, high energy density, high efficiency *liquid alkali metal storage cells*

Towards Economical and Safe Storage of Solar and Wind Energy

C. Austen Angell and Steve W. Martin



TALK OUTLINE

1. What we planned originally, and how it didn't work
2. Identifying the problems
3. Doing something about it

    (a) Changing to NaSICON separator

    (b) ***Development of liquid redox cathodes***

    (i) theoretical considerations.. The solvent basicity factor

    (ii) projecting the cell voltages

    (c) Testing the new cells

    (i) the Fe(II)/Fe(III) redox cathode (at ASU)

    (ii) the medium-temperature >100ºC, aqueous Cu cathode

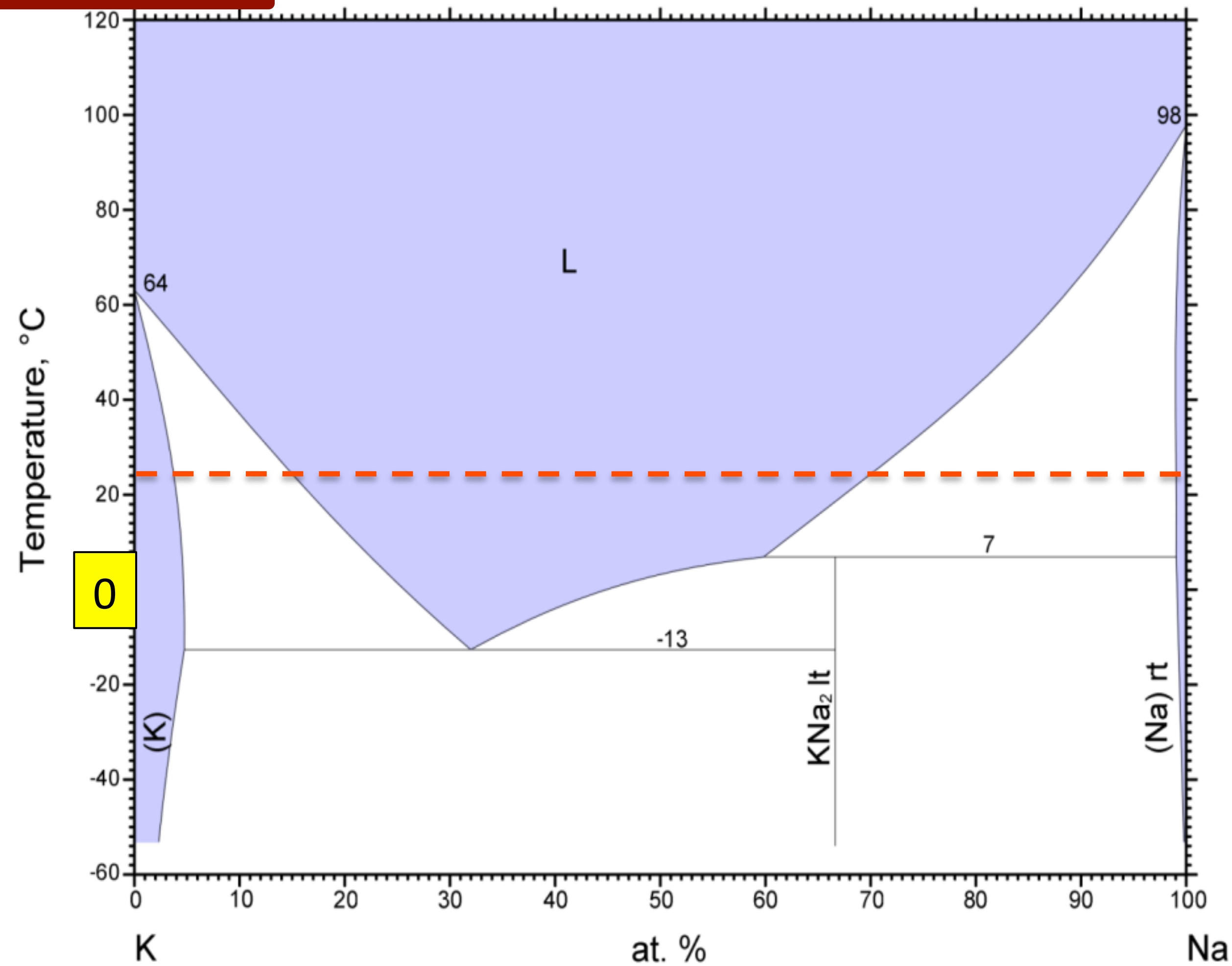
4. Future prospects

Original plan (optimistic)

Na-K phase diagram

Use
(i) alkali metal alloys and
(ii) ionic liquid electrolytes

To lower the working temperature of the liquid alkali metal storage cells (like ZEBRA) to ambient temperature.



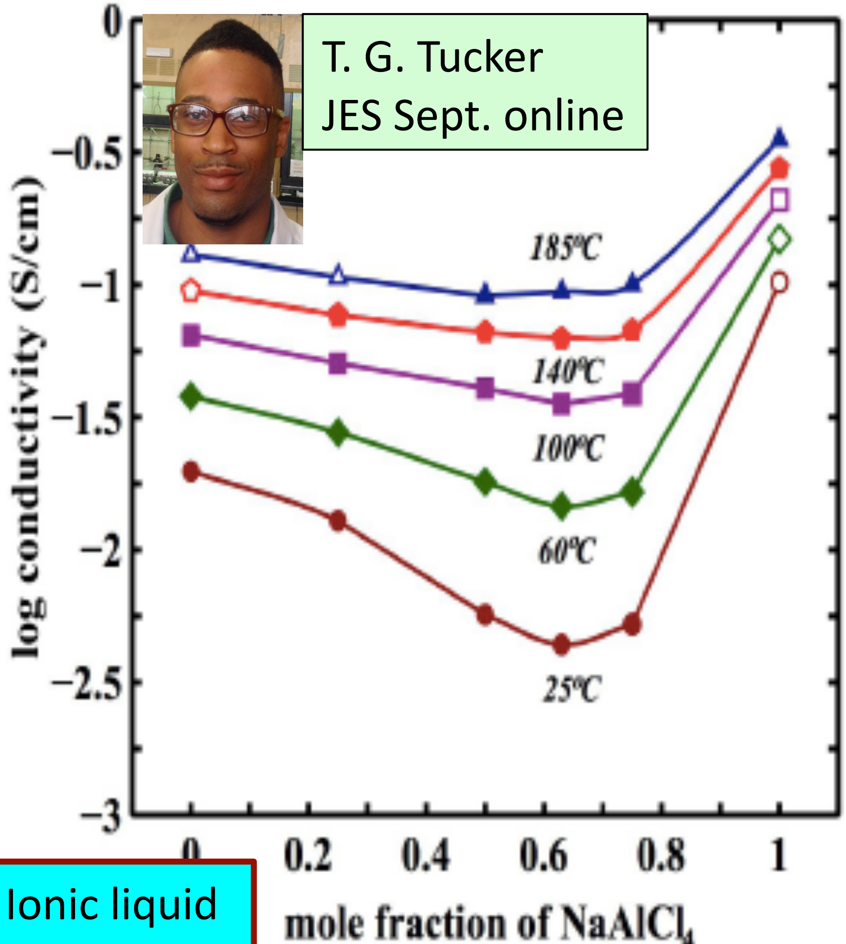
Na-K phase diagram showing ambient liquids, 13 to 72at.% sodium, (from ASM 90146).

Na^{+} - rich electrolytes, high conductivity, σ ~0.1 S/cm @ T ~100

At ASU Results:

Sodium ion trapping confirmed, but not too serious > 100ºC

T. G. Tucker
JES Sept. online



Ionic liquid
[EMI][AlCl$_4$-

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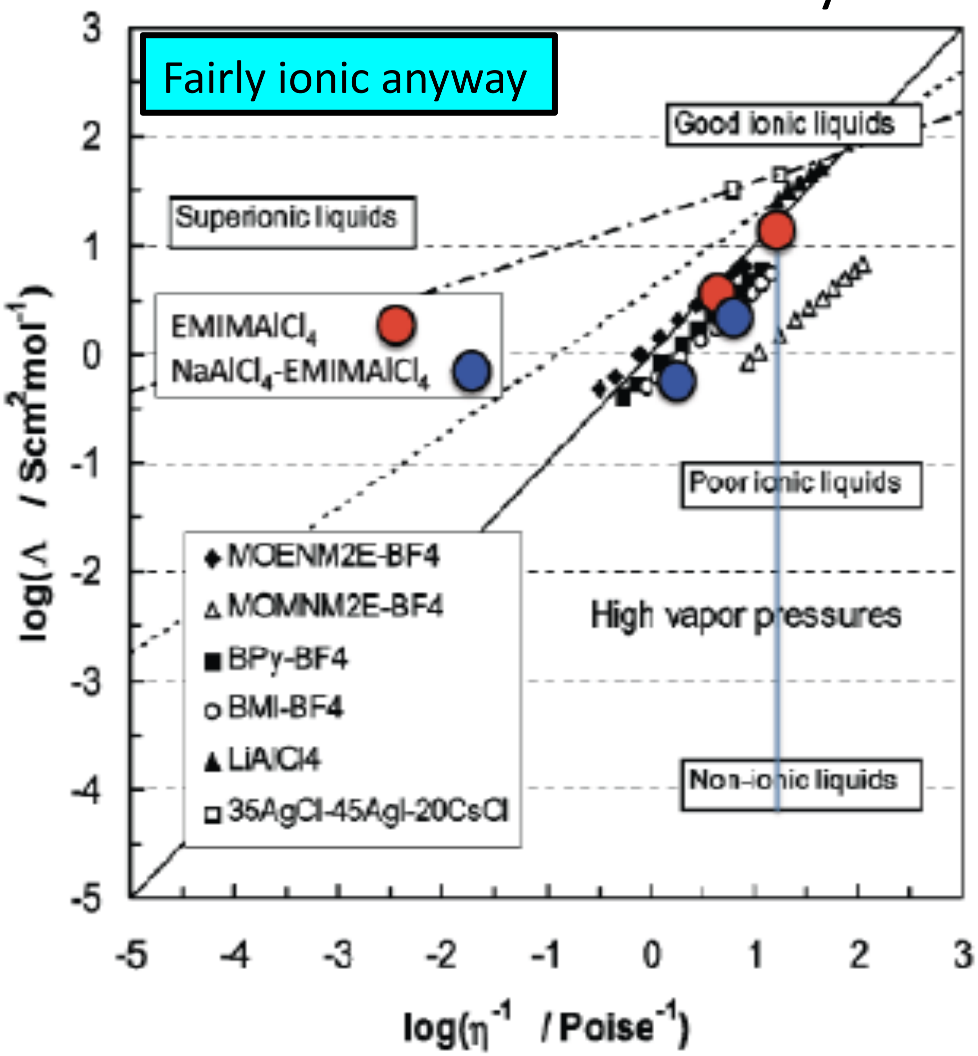
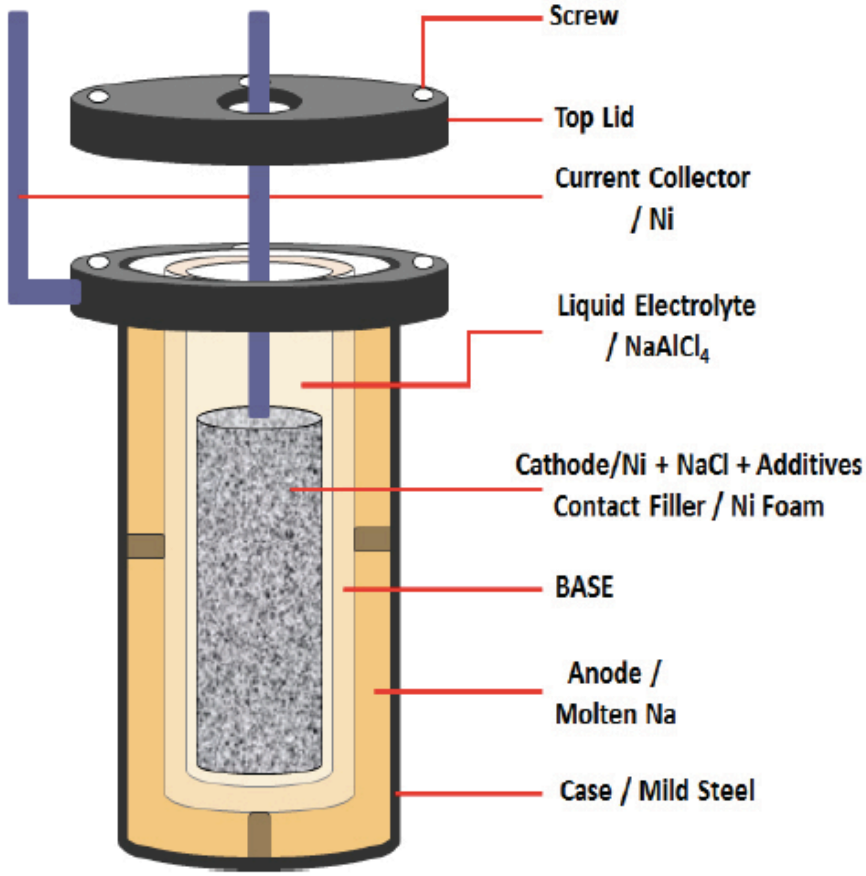
Walden Plot for ionicity

Fairly ionic anyway

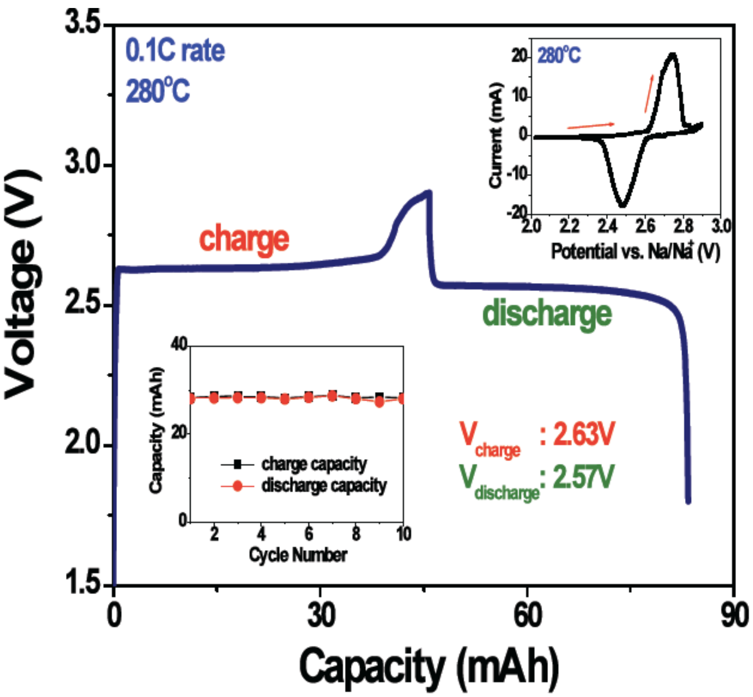


At ISU - a standard design Zebra cell for testing new ingredients under known conditions

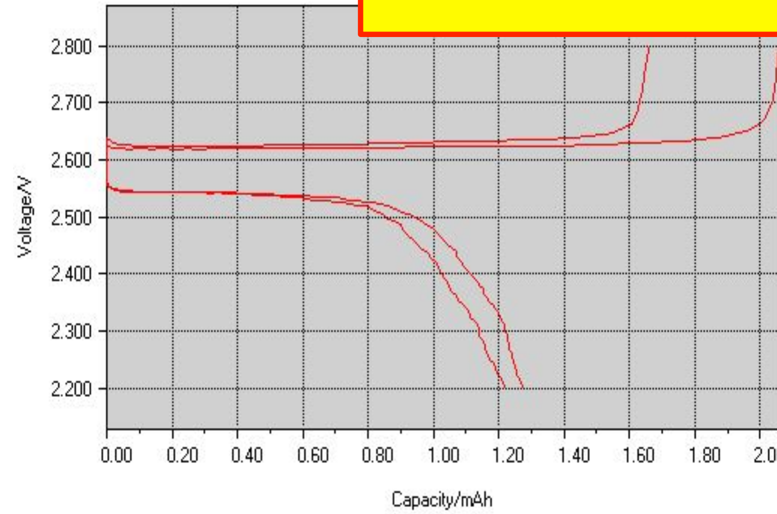


At ISU — Results in Zebra cells — At ASU

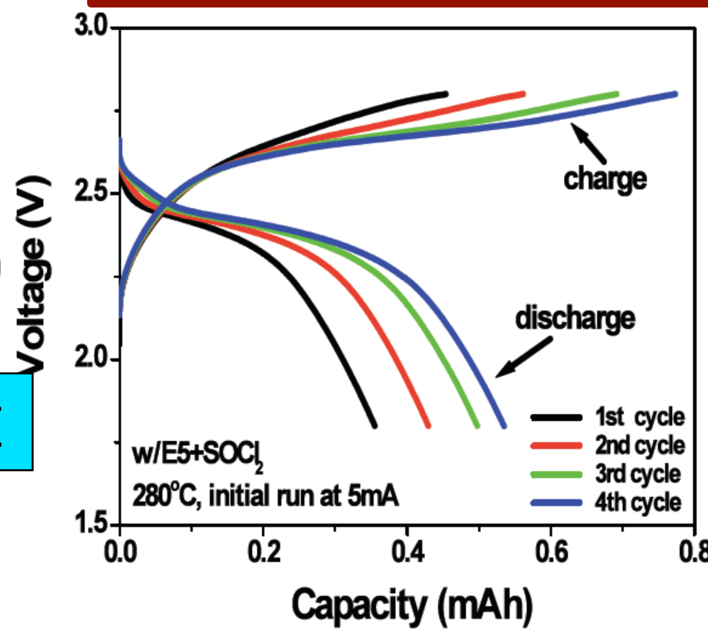
Tube cell design with a Standard Catholyte



EXCELLENT PERFORMANCE

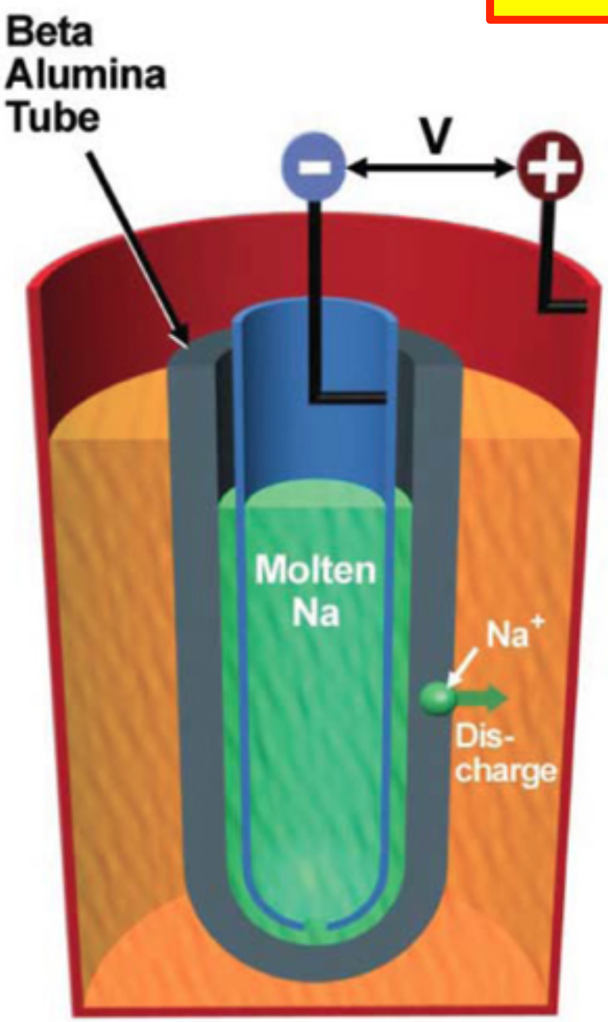


But with Low Temp IL Catholyte



Very Low Capacity

Testing at ISU using standard design

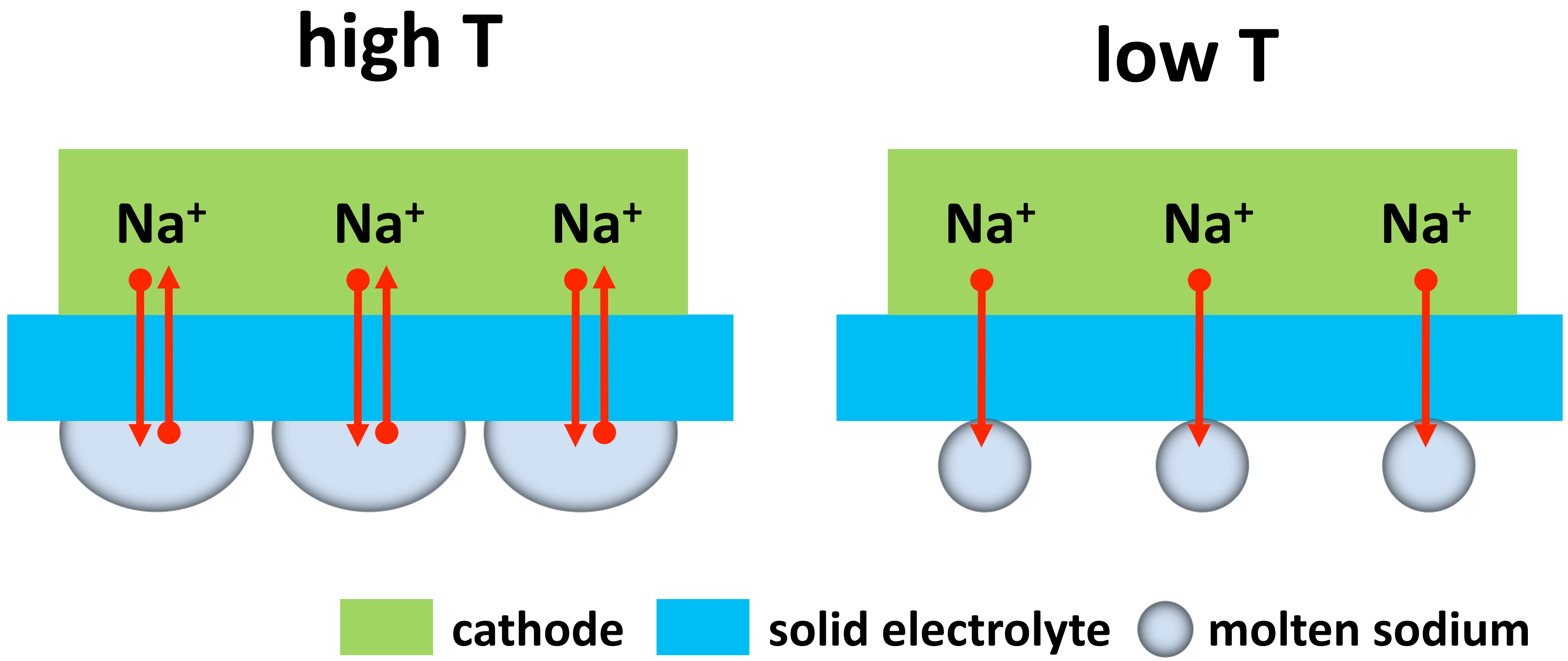


Possible problems

- Sodium doesn't wet ceramic at low T
- Beta alumina doesn't conduct well enough at low T
- $NiCl_2$ kinetics inadequate at low T
- Only single crystal β" alumina tolerates both Na and K ions

Traditional tublar ZEBRA battery works over 300 ℃

Is the problem in the "wettability" of the solid electrolyte by sodium?

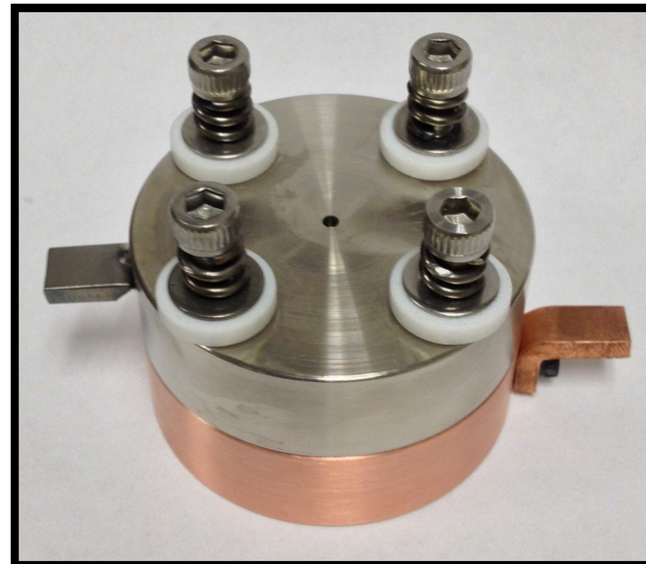


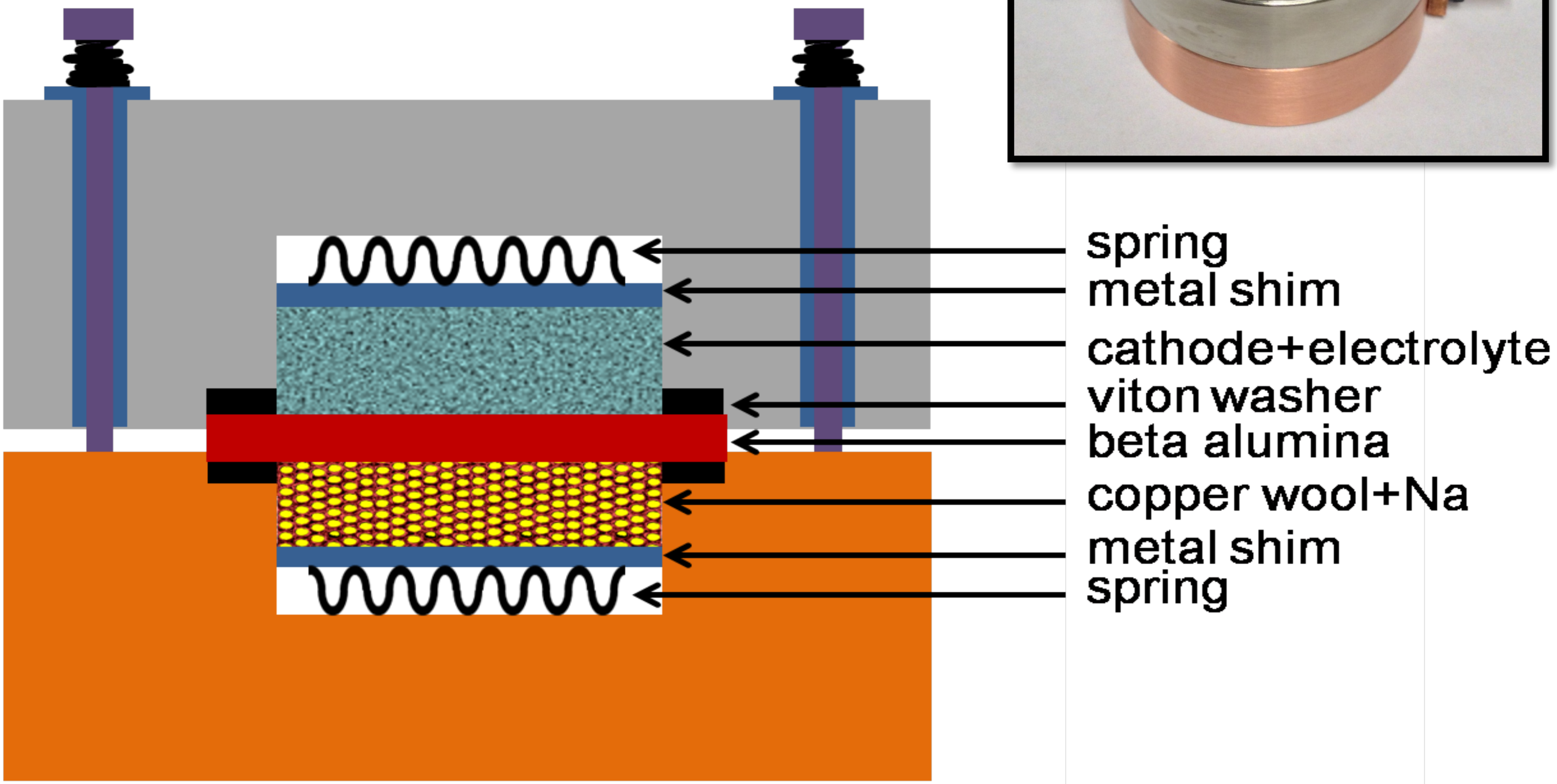
Schematic for wetting of sodium on beta alumina/Nasicon at different temperature, (left) good wettability at high temperatures and Na^+ can be transferred reversibly; (right) the wettability is poor at low temperatures and the Na^+ can only transfer from cathode to anode, Na^+ can not go back to cathode side.

Demountable flat panel design

Leigang Xue

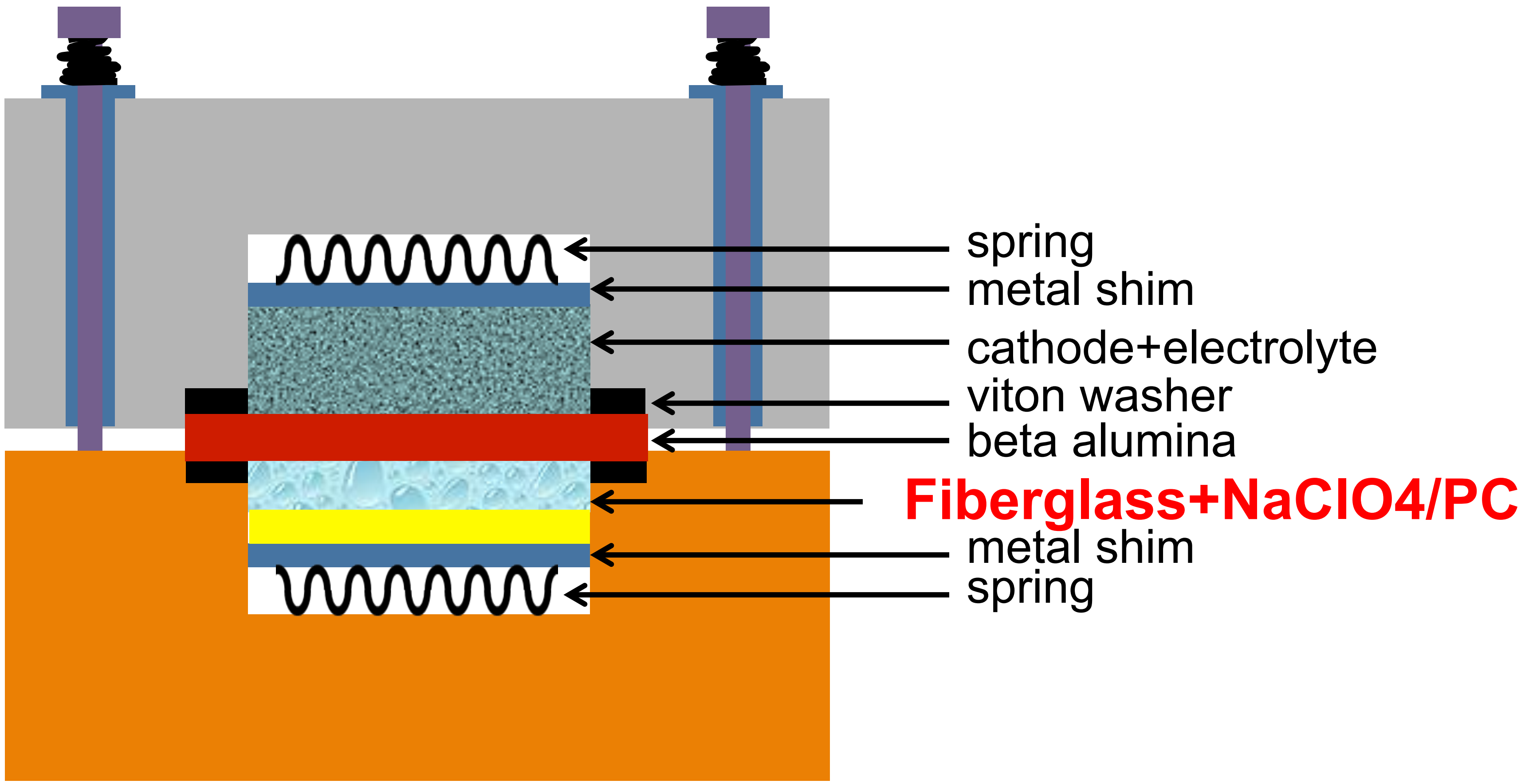
At ASU





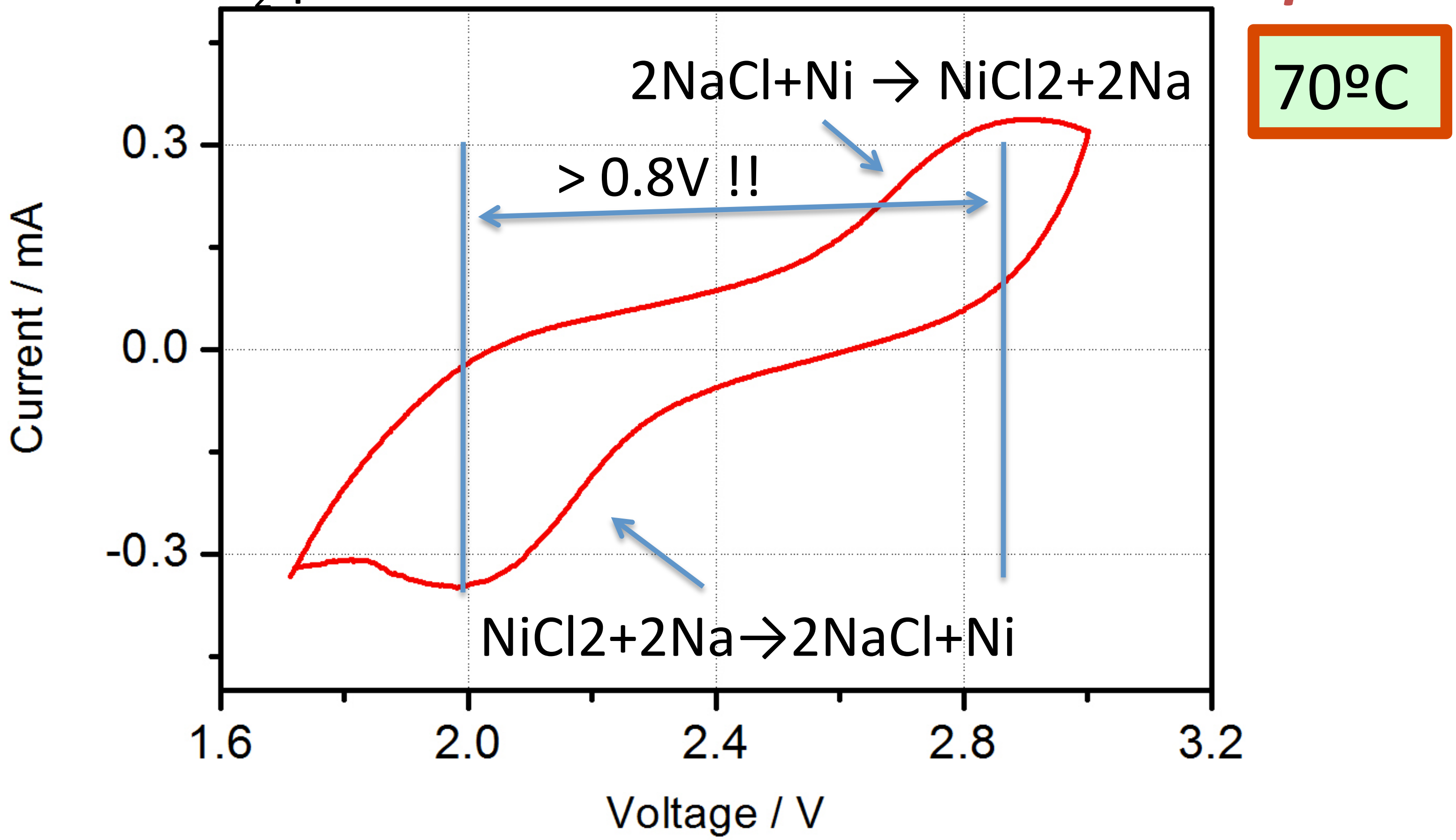
WETTING Test: **Use a low surface tension auxiliary Na^+-carrying solution ($NaClO_4$/PC) to wet the NaSICON**

(as in the recent "hybrid" aqueous cathode cells)



Now, with NaClO4/PC to wet Nasicon

We can observe a cycle, but the kinetics are terrible ! This has to be an $NiCl_2$ problem. The solution ? ***Abandon ship !***



Cyclic voltammograms of ZEBRA cell with Nasicon, 1 M NaClO4 in PC is used to wet nasicon. *Clear oxidation and reduction peaks of Ni2+/Ni* can be see at about 2.8 and 2.0 V. 70 ℃

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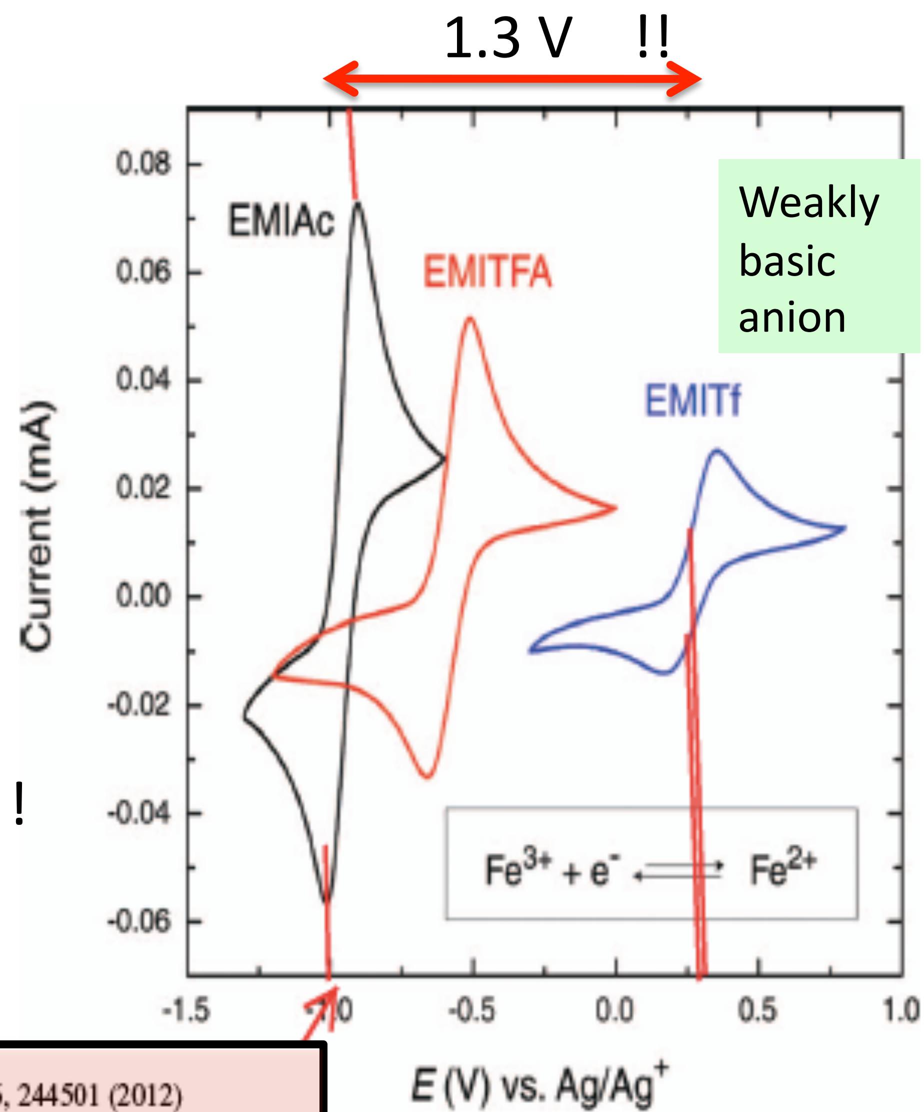
So we need

1. Liquid cathode process that is reversible
2. Na-wettable separators

Recent literature:
the $Fe(II) \Longleftrightarrow Fe(III) + e^-$
equilibrium in ionic liquid media:

Redox potential is highly dependent on solvent anion basicity. $\Delta E = 1.3$ V !

Using standard data, $Na + Ag^+ \Longleftrightarrow \mathbf{Na^+} + Ag$
$E_{cell} = 3.5$ V



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Ionic liquids as oxidic media for electron transfer studies

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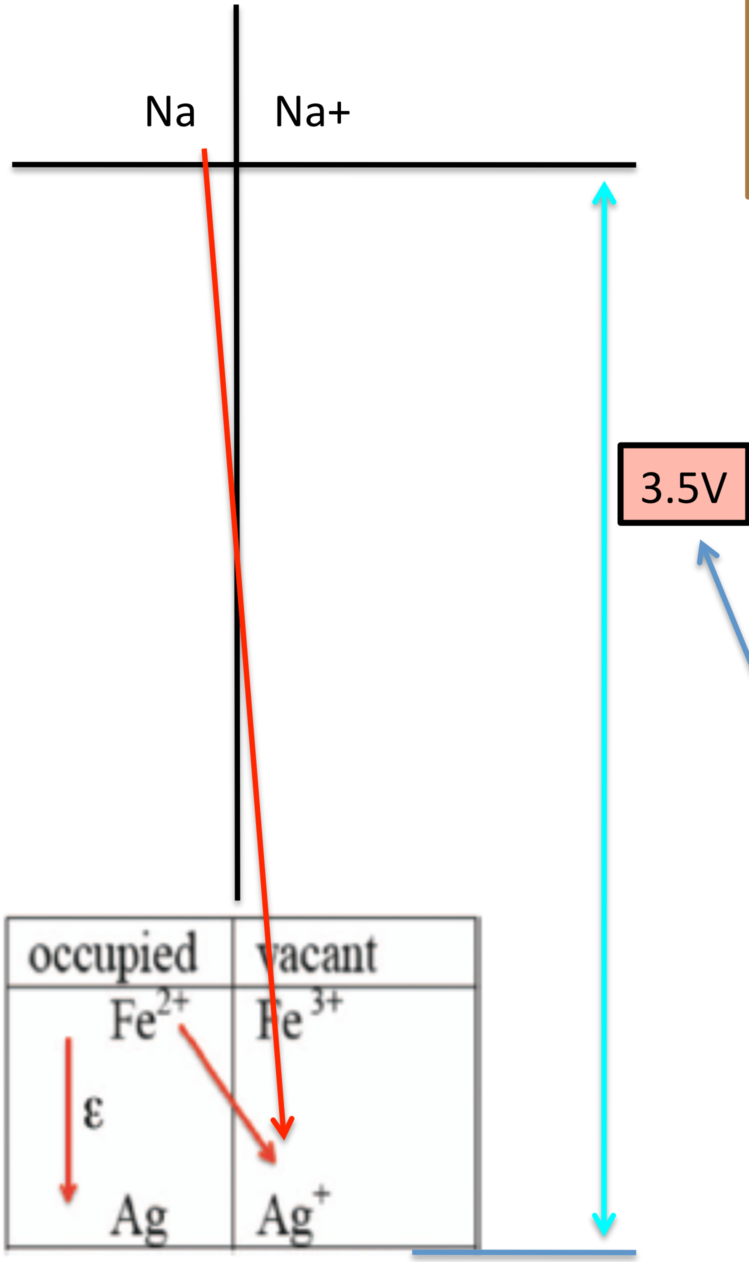
Evaluating the possible cell emf



SCHEME 1.

$$Na + Fe(III) \underset{charge}{\overset{discharge}{\rightleftharpoons}} Na^{+} + Fe(II)$$

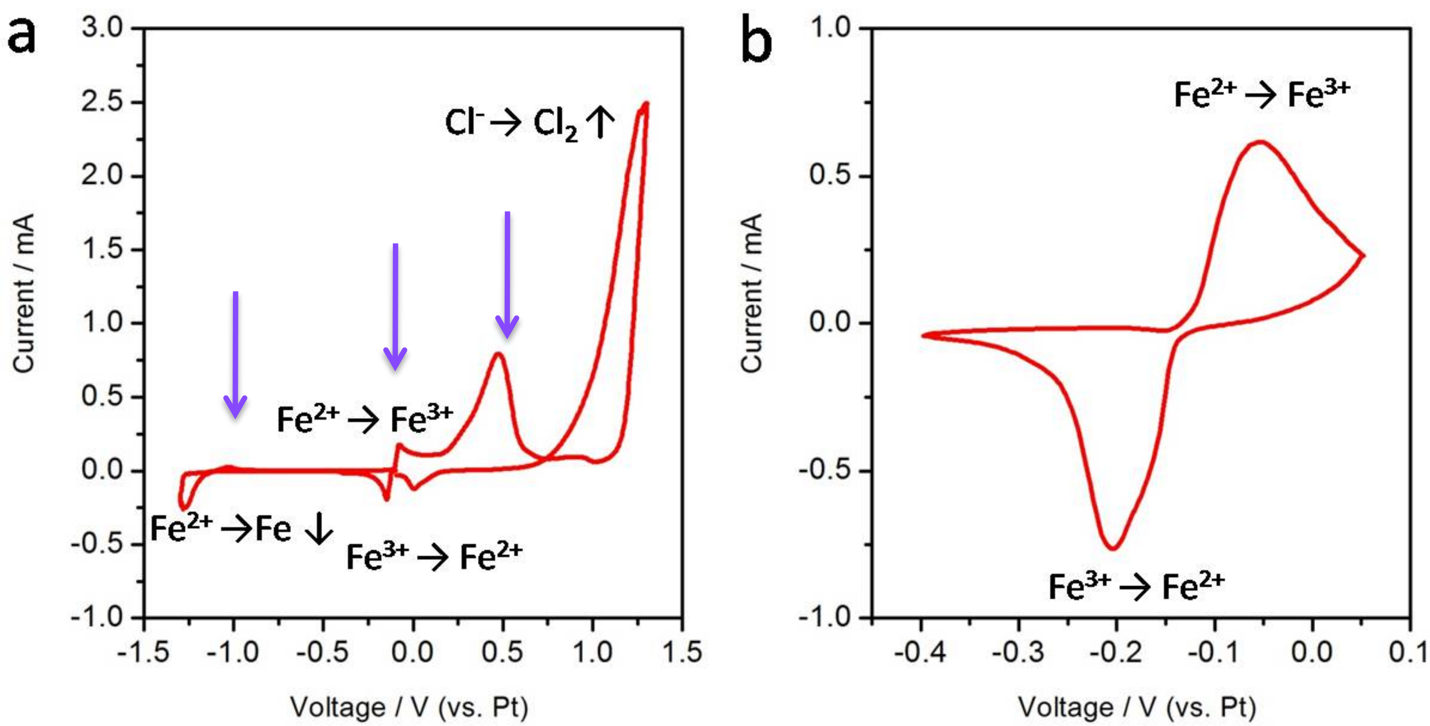
From standard textbook tables for a well-known oxidic medium, ***water***

In acid medium, silver will oxidize ferrous iron to ferric meaning a Na/Fe(redox) cell with voltage above 3.5 V should be possible : (analog of LiFePO4)

Testing the concept with a CV (three electrode cell) and $EMIFeCl_4$-$NaAlCl_4$ (1:1)

$$Na + EMIFeCl_4 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} [EMI^+][FeCl_3^-] + NaCl$$

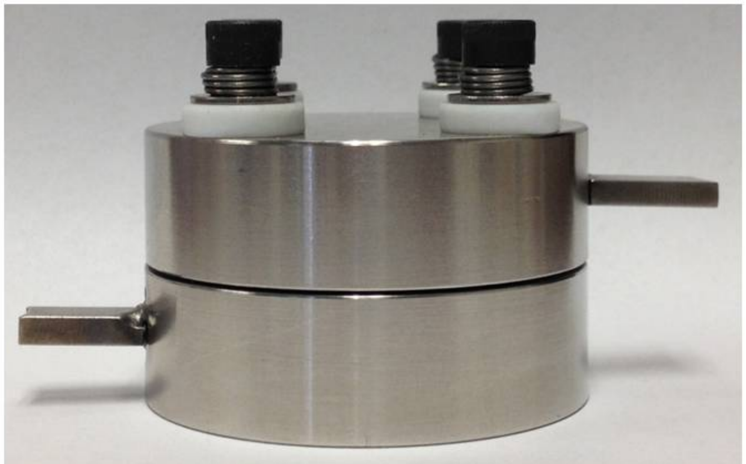
AlCl4- is the anion of a super acid.. i.e. it is an extremely weak base



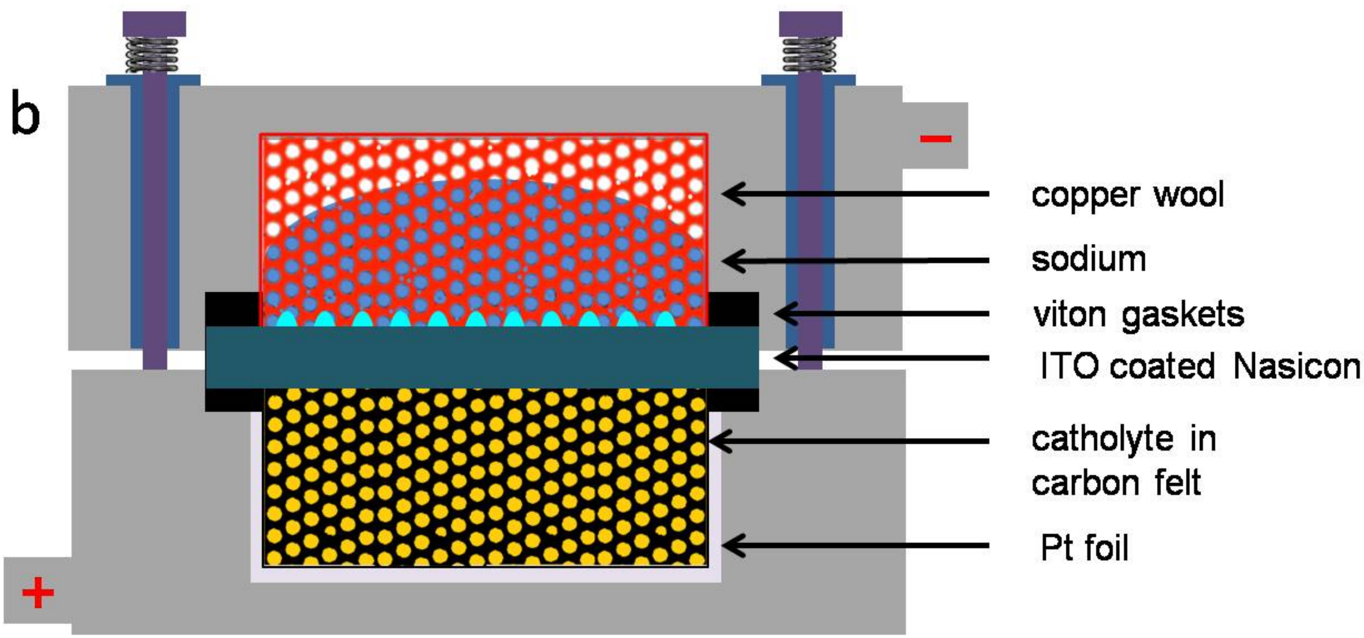
Cyclic voltammograms of EMIFeCl4-NaAlCl4 with different voltage range, (a)-1.3~1.3 V; (b) -0.4~0.05 V. Pt as reference electrode, scan rate 10 mV s-1, *T* = 180 °C.

And now the cell, and the wetting problem

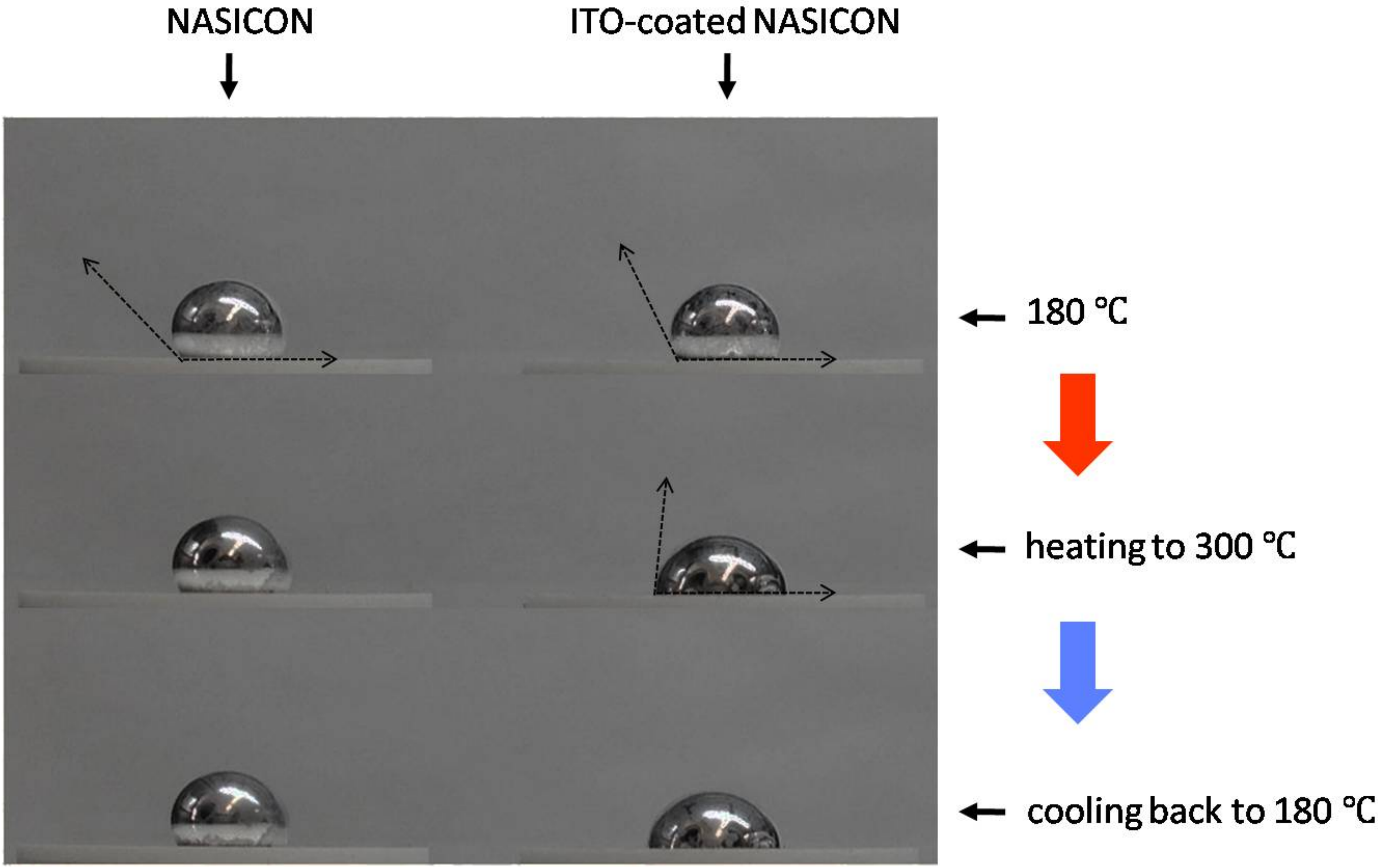
a



b



Solving the wetting problem



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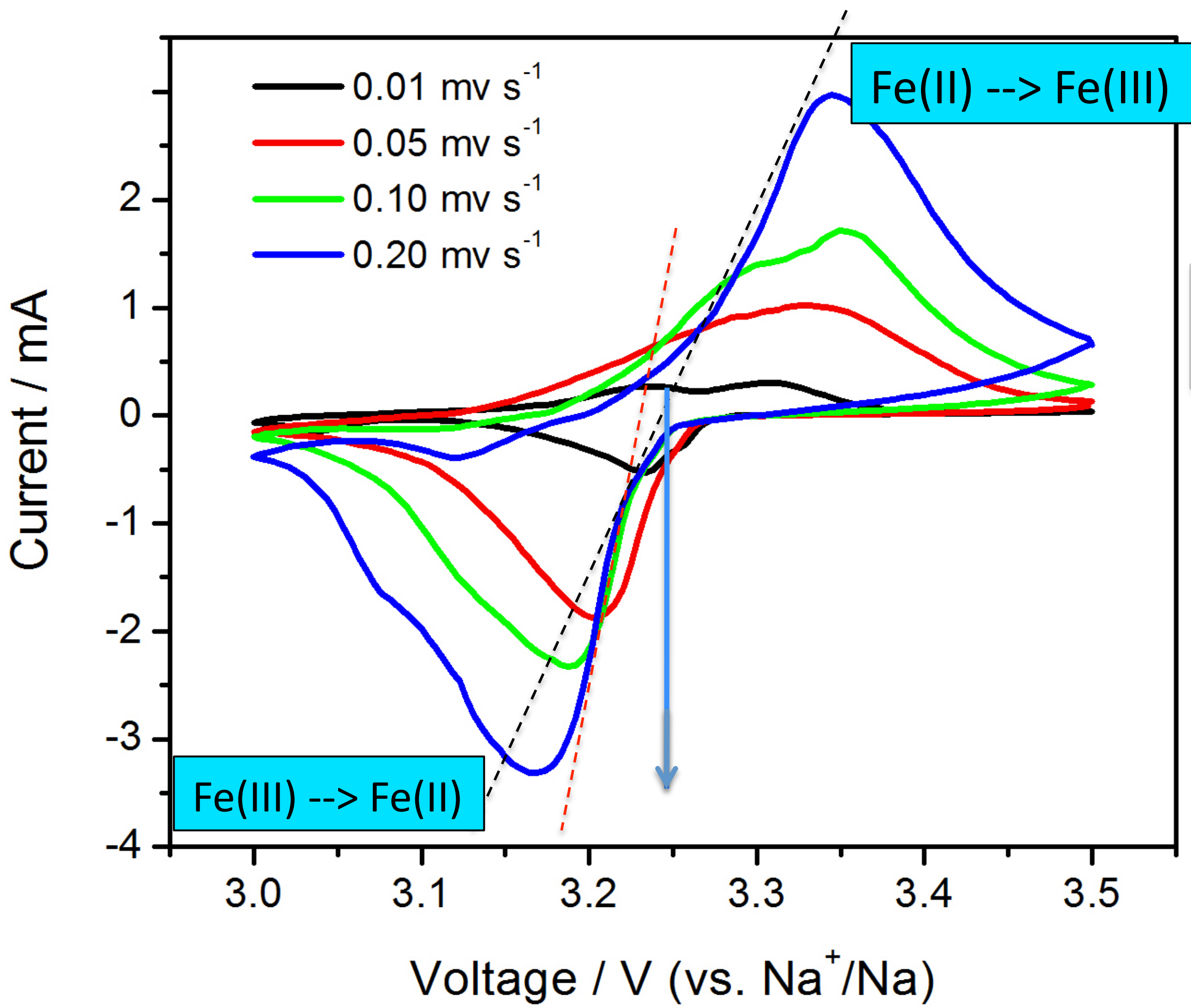
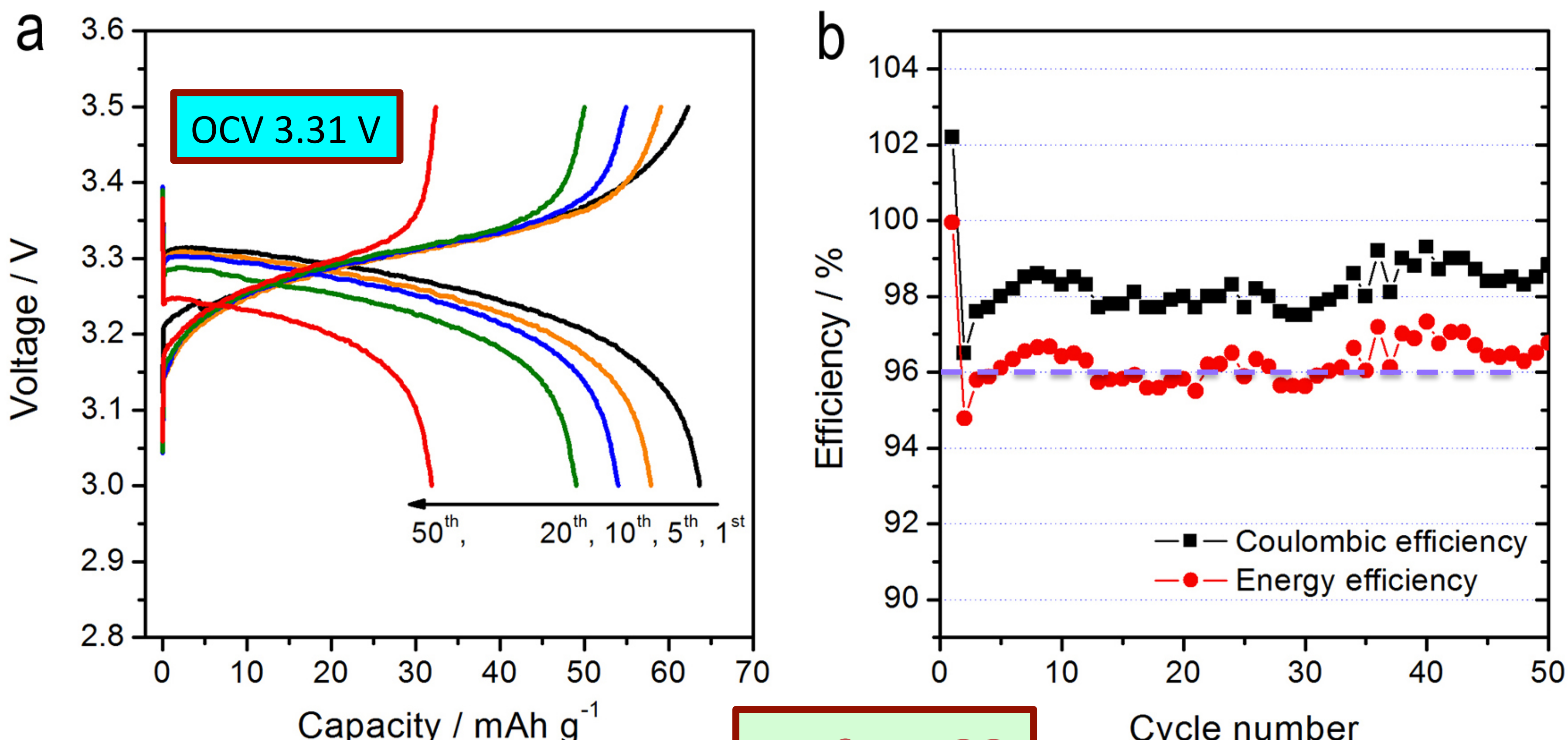
Now the cell test. CV in the cell and the cell voltage



3.25 V !!

The cell performance. Capacity is 70% of theoretical , but fading over 50 cycles

But the energy efficiency is outstanding > 96%



Safety ??

Safety issues: what happens if the ceramic cracks and direct mixing of catholyte and liquid sodium occurs?

Let's see.... (movie in low O_2 dry-box

High safety against internal failure, c.f. Na-S

Improvements to be tried

Avoid the formation of, and redissolution of NaCl

$$Na + EMIFeCl_4 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} [EMI^+][FeCl_3^-] + NaCl$$

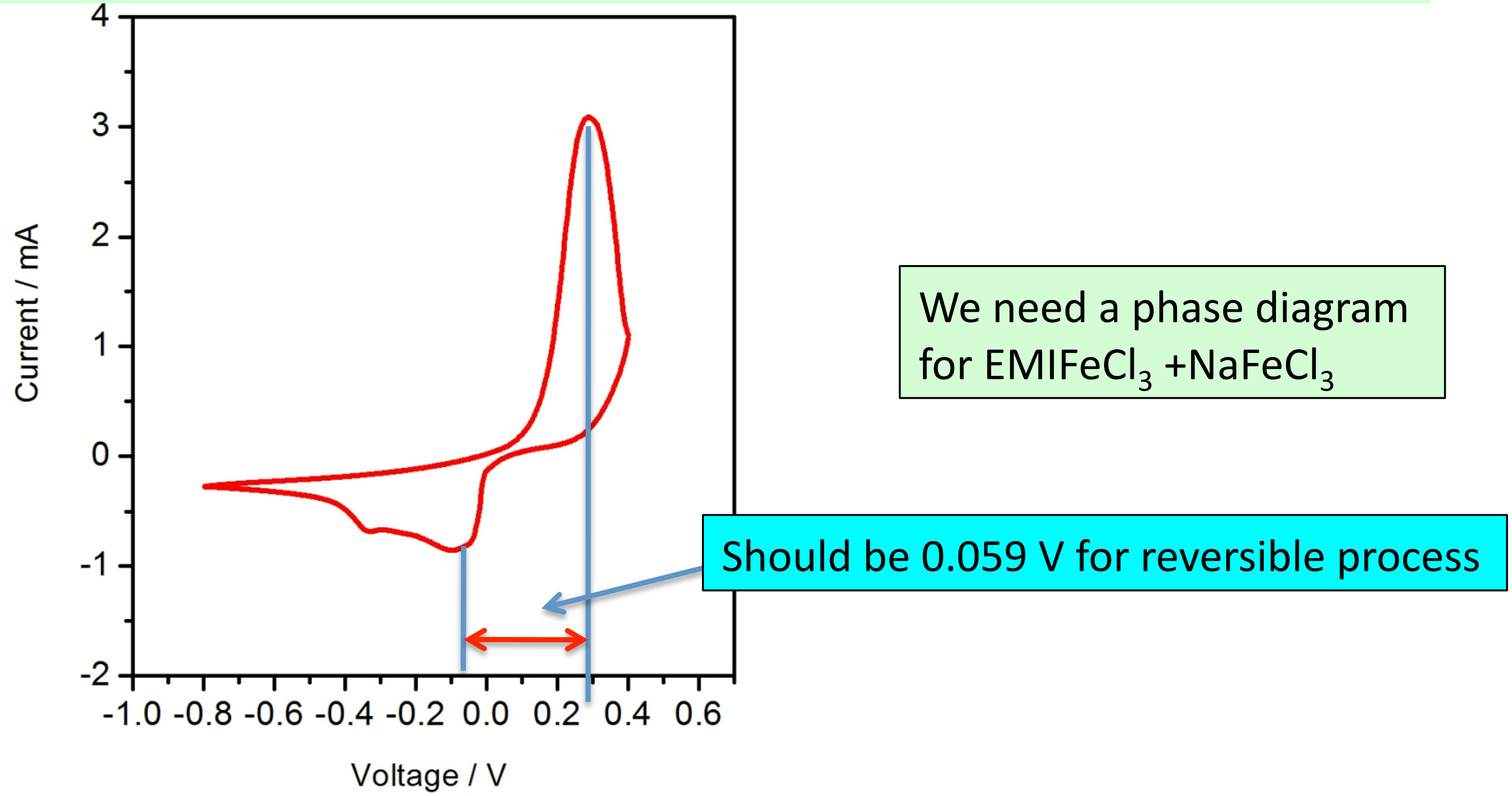
by using an extra mole of $FeCl_3$ (also should increase the cell capacity)

$$Na + EMIFe_2Cl_7 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} [EMI^+][FeCl_3^-] + NaFeCl_4$$

Extra Lewis acid raises the cell voltage to **3.7 V**

Cathode: $EMIFe_2Cl_7$-$NaAlCl_4$ (1 : 0.2)

This should have an all liquid first stage, and **a second stage** that increases the capacity but is slower because of NaCl formation



We need a phase diagram for $EMIFeCl_3$ +$NaFeCl_3$

(+) $EMIFe_2Cl_7 + e^- + Na^+ \rightarrow EMIFeCl_3 + NaFeCl_4$

$NaFeCl_4 + e^- + Na^+ \rightarrow NaFeCl_3 \downarrow + NaCl \downarrow$

(-) $Na \rightarrow Na^+ + e^-$

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Hao Liu and Steve W. Martin at ISU; the >100ºC aqueous copper cathode cell

- Anode: empty
- Cathode: 5.5 M NaCl + 5.5 M $ZnCl_2$ aqueous solution, copper wool filling
- Total cell reaction:

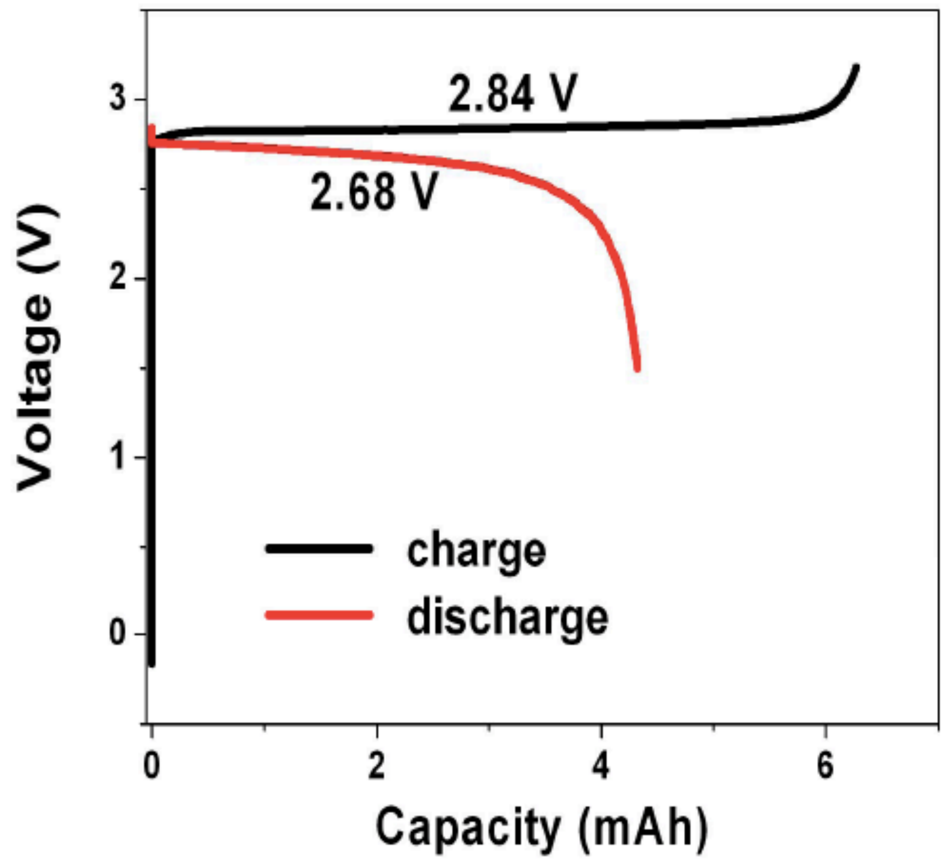
$$2NaCl + Cu \Leftrightarrow 2Na + CuCl_2$$

charging

theoretical voltage:

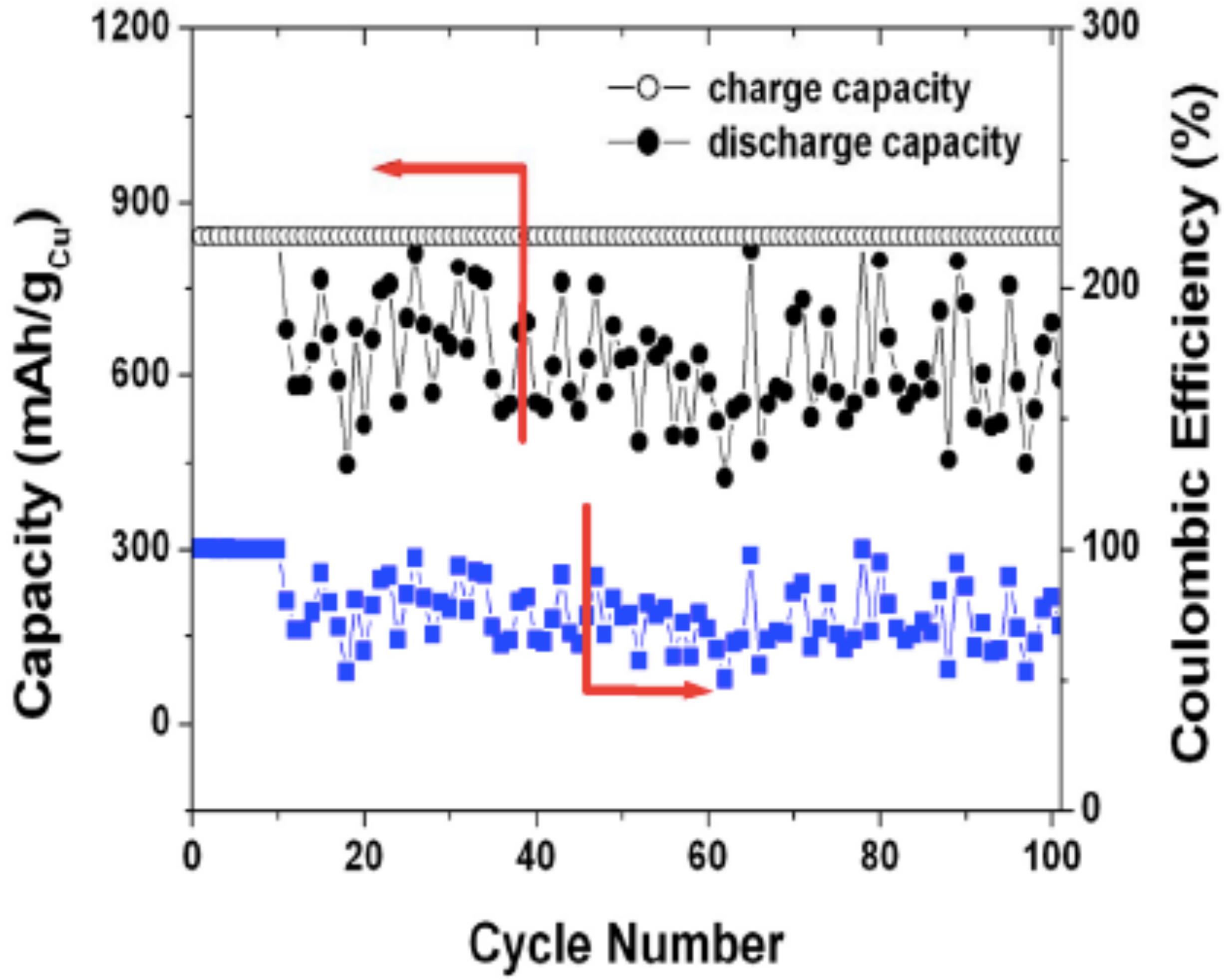
2.805 V @ 103ºC and 1s charging time

The planar cell (identical to the ASU cell), and the initial tests



2.7 V OCV with little charging overvoltage: some side reaction?

Noisy data but no capacity or coulombic efficiency fade



- Average coulombic efficiency is about 80% in 100 cycles.

Other degrees of freedom

1. The ionic liquid Fe(redox) cell
   (i) Other transition metal redox couples
   (ii) Other ionic liquid cations of higher chemical stability.
   (iii) Other lower cost Na wetting agents – Fe...

2. And the >100ºC aqueous brine cell being tested at ISU
   (i) Other transition metal redox couples
   (ii) Other (lower cost, non-toxic) spectator salts for vapor pressure lowering
   (iii) Other lower cost Na wetting agents – Fe...

Summary

1. ZEBRA cell shown impractical at low temperatures

2. New liquid cathode cells developed that work well in the low temperature range

   (a) Na- Fe (redox) cell in ionic liquid electrolyte at 180ºC OCV = 3.3 -3.5 V
   high energy efficiency, cheap and fail-safe

   (b) Na-Cu cell at 103ºC OCV = 2.8 V
   Potential to reach really high C rates. Many degrees of freedom to explore